

**METHOD OF DETERMINING A REMAINING OPERATING TIME OF
A POTENTIOMETRIC MEASURING PROBE, APPARATUS FOR
PERFORMING THE METHOD, AND USE OF THE APPARATUS**

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BACKGROUND OF THE INVENTION

Technical Field

The present invention relates to a method of
10 determining a remaining operating time of a potentiometric
measuring probe containing an electrolyte as well as a
primary reference element and a secondary reference element,
wherein the reference elements are arranged so that an
electrolyte deficiency advancing from an opening in the
15 measuring probe arrives at the secondary reference element
before it reaches the primary reference element. In
addition, the scope of the invention also includes an
apparatus for performing the method, as well as the use of
the apparatus.

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State of the Art

A widely used kind of measuring probe for
potentiometric measurements of ion concentrations or redox
potentials is equipped with a diaphragm of porous material.
25 The diaphragm serves to bring a reference electrolyte and/or
a bridge electrolyte, normally in the form of a liquid

contained inside the measuring probe, into contact with a test solution. Particularly in chemical or micro-biological process-monitoring and process-control applications, the diaphragm may be subject to contamination which can falsify the results of the measurements.

Another measuring probe, disclosed in DE 34 05 431 C2, has no diaphragm and is significantly less prone to contamination. It has a housing of an electrically insulating material with at least one enclosed space containing a reference element and an electrolyte. The housing has at least one opening through which the electrolyte can be brought into contact with a liquid solution on the outside of the housing, i.e., with the medium on which a measurement is to be performed. The enclosed space inside the housing is filled with an ion-permeable, micro-porous, high-viscosity polymer substance which, in combination with the electrolyte, forms a filler mass of the measuring probe. This type of construction assures that the electrical potential measured at the reference element is highly constant even if the solutions being measured are strongly contaminated. In addition, the measuring probe can sustain pressure levels significantly in excess of 10 bar.

Measuring probes of the foregoing description are known to have the problem that, as the cumulative operating time of the probe advances, the electrolyte that is initially

contained in the polymer substance will to an increasing degree migrate into the test solution, resulting in a progressively spreading electrolyte deficiency in the polymer substance inside the housing. The increasing electrolyte deficiency in the polymer substance is also referred to as the aging process of the measuring probe and produces the undesirable effect that, when the electrolyte deficiency eventually reaches the reference element, there will be a change in the electrical potential measured at the reference element. To avoid the risk of erroneous measuring results, it is therefore necessary to monitor the aging process of the measuring probe. In particular, it should be possible to detect sufficiently in advance when the electrolyte deficiency is approaching the reference element, i.e., at a point when there is still an adequate amount of time left during which the probe can continue to operate.

According to DE 34 05 431 C2, the problem of detecting the advancement of the electrolyte deficiency can be solved by using an electrolyte consisting of a suspension of homogeneously distributed particles of a neutral salt with ions of equal transport number in an aqueous solution of the neutral salt. The polymer substance and the neutral salt suspension together form a gel that has a turbid appearance due to the salt particles in suspension. The state of aging of the measuring probe can be visually detected, as the turbidity disappears progressively with the advancement of

the aging process. The reason for the decrease in turbidity is that the suspended neutral salt particles continuously pass into solution until a final state has been reached where there are essentially no suspended particles left, so that as
5 a result the turbidity is strongly diminished. It has been found that in the aging process, a clearly visible boundary develops between a turbid portion of the gel where the neutral salt particles are homogeneously suspended and a comparatively clear portion where the neutral salt particles
10 have passed into solution. The state of advancement of the boundary from the opening in the housing towards the reference element can be determined through visual observation. Based on a current position and speed of advancement of the boundary, it is possible to draw
15 conclusions about the current state and speed of aging and thus predict the remaining operating time of the measuring probe.

However, the measuring probe according to DE 34 05
20 431 C2 has several drawbacks. To monitor the state of aging and determine the remaining operating time of the probe, it is necessary to be able to clearly see inside the enclosed space of the measuring probe. This precludes the use of a non-transparent material for the housing, and it also
25 presents a problem with a transparent housing if the latter becomes contaminated by surface deposits. A further severe problem occurs if the gel in the enclosed space becomes

discolored or contaminated, e.g., by the infusion of colored substances or infiltration of dirt particles from the test solution, which could make it practically impossible to visually detect the boundary of the electrolyte deficiency.

5 It also has to be counted as a drawback that, in order to make the boundary visible, the electrolyte needs to be a suspension of homogeneously distributed particles of a neutral salt with ions of equal transport number in an aqueous solution of the neutral salt, a condition that
10 excludes other kinds of electrolytes from being used in the measuring probe.

OBJECT AND SUMMARY OF THE INVENTION

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The object of the present invention is to propose an improved method of determining the remaining operating time which is free of the disadvantages named above. Further objects of the invention are to provide an apparatus for
20 performing the method, and to propose a use for the apparatus.

The first of the foregoing objectives is achieved by the method of the present invention, which serves to
25 determine how much operating time is left in a measuring probe containing an electrolyte as well as a primary reference element and a secondary reference element, wherein

the reference elements are arranged so that an electrolyte deficiency advancing from an opening in the measuring probe arrives at the secondary reference element before it reaches the primary reference element. Under the inventive method, the difference between the respective electrical potentials of the primary reference element and the secondary reference element is monitored against a predefined tolerance criterion. When the result of the monitoring ceases to meet the tolerance criterion, the elapsed operating time is determined from the point when the probe was put into operation and used as a basis for the calculation of the remaining operating time.

With the inventive method, the enclosed space in the measuring probe does not need to be accessible to visual observation. Consequently, the method can also be used in particular for measuring probes with a non-transparent housing, or for measuring probes that are installed in a probe-holder assembly. In addition, the method can also be used in measuring probes where the probe housing is covered with contaminants, as may be the case if the measuring probe is used for dirty or foamy sample solutions. Also, as the boundary of the electrolyte deficient region no longer needs to be visible, the range of applications for the inventive method is further expanded because the choice for the electrolyte is not limited by the requirement to use a suspension of homogeneously distributed particles of a

neutral salt with ions of equal transport number in an aqueous solution of the neutral salt. In particular, the inventive method can also be used for measuring probes with an electrolyte consisting of a saturated or near-saturated solution of a neutral salt in an appropriate solvent, e.g., a near-saturated solution of potassium chloride in water. With the concept of determining the elapsed operating time from the point when the probe was put into operation to the point where the tolerance criterion ceases to be met and using the elapsed operating time as a basis for calculating the remaining operating time, the speed of aging of the measuring probe under the actually used operating conditions is taken into account, which leads to a more reliable prediction of the remaining operating time.

The apparatus according to the invention includes a potentiometric measuring probe with an electrolyte as well as a primary reference element and a secondary reference element, wherein the reference elements are arranged so that an electrolyte deficiency advancing from an opening in the measuring probe arrives at the secondary reference element before it reaches the primary reference element. The apparatus further includes means for determining the elapsed operating time from the point when the measuring probe was taken into operation, means for monitoring the difference between the electrical potentials of the primary reference element and the secondary reference element, and means for

calculating the remaining operating time of the measuring probe. The result of the calculation can be shown in a display device and/or processed further through conventional means.

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The apparatus according to the invention can be used advantageously in process-monitoring and/or process-control applications.

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According to an advantageous embodiment of the invention, a detected violation of the tolerance criterion triggers a warning signal. The warning signal can for example take the form of an optical and/or acoustical indication, particularly a message that appropriate steps should be planned, such as servicing or replacement of the measuring probe.

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A further embodiment of the inventive method requires a substantially continuous monitoring of the electrical potential difference. As an alternative possibility, the potential difference can be monitored at intermittent time intervals, for example periodically.

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A further developed version of the inventive method includes signal-filtering in the monitoring of the electrical potential difference. This is particularly advantageous if

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the potential difference as a function of time is subject to fluctuations and noise.

In principle, there are several different possibilities to set a tolerance criterion or to formulate a definition as to what should be counted as a violation of the tolerance criterion. According to a first definition, a violation of the tolerance criterion occurs at the moment where the absolute amount of the potential difference leaves a predetermined tolerance range. Under another definition, violations of the tolerance criterion are defined as events where the absolute value of the first time derivative of the potential difference traverses one or more predefined tolerance values. This implies that the potential difference is monitored as a function of time. As a further possibility, violations of the tolerance criterion can be defined as events where the absolute value of the second time derivative of the potential difference traverses one or more predefined tolerance values.

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In principle, there are several ways to calculate the remaining operating time of the measuring probe by using a base time period representing the amount of operating time elapsed from the point when the measuring probe was taken into operation to the time of the violation of the tolerance criterion. As an example, the remaining operating time can be calculated by multiplying the base time period with a

predefined factor. Under a further advantageous concept of the invention, after detecting a violation of the tolerance criterion, the potential difference is monitored against a predefined alarm criterion, and subsequent to a violation of the alarm criterion the remaining operating time is set to zero. As an additional advantageous feature, a violation of the alarm criterion triggers an alarm signal. The embodiments that include an alarm criterion provide an additional measure of operating safety, particularly against the risk of continuing to use the measuring probe after the electrolyte deficiency has already reached the primary reference element, which could happen in a case where an indication of the remaining operating time was not noticed or was disregarded.

The concepts described above for the tolerance criterion and for defining what constitutes a violation of the tolerance criterion are analogously applicable to the alarm criterion.

BRIEF DESCRIPTION OF THE DRAWINGS

A detailed description of embodiments of the invention will be presented further below with references to the drawings, wherein:

Figure 1 represents a lengthwise sectional view of a measuring probe that is configured as a reference electrode;

5 Figure 2 represents a lengthwise sectional view, shortened by cutting out the mid-portion, of a measuring probe with a lengthened path of advancement of the electrolyte deficiency;

10 Figure 3 represents a lengthwise sectional view of the upper part of a further measuring probe with a lengthened path of advancement of the electrolyte deficiency;

Figure 4 represents an example for the potentials of the two
15 reference elements as well as the potential difference as functions of the elapsed operating time;

Figure 5 represents the absolute amount of the potential
20 difference of Figure 4 as a function of the elapsed operating time;

Figure 6 represents an example for the absolute amount of
the first time derivative of the potential
25 difference as a function of the elapsed operating time; and

Figure 7 represents an example for the absolute amount of the second derivative of the potential difference as a function of the elapsed operating time.

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DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Figure 1 illustrates a measuring probe configured as a reference electrode with a tubular housing 2, usually referred to as the electrode shaft and consisting of an electrically insulating material, e.g., glass or a polymer material such as a polyarylether ketone (PAEK), in particular a polyether-ether ketone (PEEK). The housing 2 surrounds an enclosed space 4 containing a primary reference element 6, a secondary reference element 8, as well as an electrolyte 10. The housing 2 has an opening 12, so that when the measuring probe is dipped into a sample solution (not shown), the electrolyte 10 is brought into contact with the sample solution. In the illustrated example, the opening 12 is formed as a passage hole in an end portion 14 of the housing 2. The enclosed space 4 is filled with an ion-permeable, high-viscosity, micro-porous polymer material which, in combination with the electrolyte 8, forms a filler mass 16. To prevent the filler mass 16 from running out of the housing through the opening 12, the filler mass should be in a highly viscous or even solid state at the normal operating temperature range of the measuring probe. As a polymer

filler mass to meet this criterion, a copolymer of acrylamide and N,N¹-methylene-bis-acrylamide has been tried and proven.

The primary reference element 6 is configured as a
5 cartridge 18 that is open on one side and contains a primary
electrode 20 of a known potential. For example, the primary
electrode is configured as an Ag/AgCl electrode with a
chlorided silver wire 22 that is immersed in a primary
electrolyte 24. To prevent the primary electrolyte 24 from
10 running out of the open end 26 of the cartridge 18, the
primary electrolyte 24 is enclosed in the pores of an ion-
permeable, micro-porous polymer substance, preferably the
same material as in the filler mass 16. On the far side from
the open end 26, the primary reference element 6 has a plug-
15 in contact 30 that communicates with the primary electrode 20
through a conductor lead 28, e.g., a platinum wire. The
plug-in contact 30 serves to establish a connection to
circuit elements contained in the header 32 of the measuring
probe or outside of the housing. In addition, the primary
20 reference element 6 contains a sealing plug 34, e.g., of
glass or a polymer material, to prevent the plug-in contact
30 from touching the primary electrolyte 24. Instead of
having an opening 26 at the end of the cartridge 18, the
primary reference element 6 could have a lateral opening if
25 desired.

The measuring probe illustrated in Figure 1 as an example of the invention has a secondary reference element 8 that is substantially identical to the primary reference element 6. Thus, the secondary reference element 8 has a cartridge 36 with an open end 38 and a secondary electrode 40 configured as an Ag/AgCl electrode with a chlorided silver wire that is immersed in a secondary electrolyte 44. The secondary electrolyte 44 is enclosed in the pores of an ion-permeable, micro-porous polymer substance, preferably the same polymer material as in the filler mass 16. In addition, the secondary reference element 8 has a plug-in contact 48 that communicates with the secondary electrode 40 through a conductor 46, e.g., a platinum wire. The plug-in contact 48 serves to establish a connection to circuit elements contained in the header 32 of the measuring probe or outside of the housing 2. In addition, the secondary reference element 8 contains a sealing plug 50, e.g., of glass or a polymer material, to prevent the plug-in contact 48 from touching the secondary electrolyte 44.

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As may be seen in Figure 1, the primary reference element 6 and the secondary reference element 8 are positioned in the measuring probe at parallel but staggered positions, with the open end 26 of the primary reference element 6 being farther removed from the opening 12 than the open end 38 of the secondary reference element 8. As will be discussed below in further detail, the staggered arrangement

has the effect that the advancing frontal boundary 52 of an electrolyte-deficient region 54 will reach the secondary reference element 8 before it reaches the primary reference element 6.

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As a preferred choice, the electrolyte 10, the primary electrolyte 24, and the secondary electrolyte 44 contain a suspension of micro-particulate potassium chloride in an aqueous solution of potassium chloride. The proportion of suspended potassium chloride should be at least 30% and may be as high as 1500% in relation to the dry weight of the polymer substance. A preferred range is between 100% and 800%, with 200% to 400% being most preferred. Instead of an aqueous solution, it is also possible to use a part-aqueous solution of potassium chloride, for example a solution of potassium chloride in a mixture of water and glycerin or ethylene glycol. This has the effect of reducing the partial vapor pressure of the water, which is desirable especially in applications at elevated temperatures. Alternatively, the electrolyte 10 and/or the primary electrolyte 24 and/or the secondary electrolyte 44 could form a solid-phase electrolyte together with the polymer substance.

As the state of aging of the measuring probe progresses with the increase in accumulated operating time, an increasing portion of the electrolyte 10, i.e., of the potassium- and chloride ions initially contained in the

filler mass 16, migrates into the sample solution. As a consequence, an electrolyte-deficient region 54 develops in the enclosed space 4, with a frontal boundary surface 52 of the region 54 advancing in the direction from the opening 12 towards the interior of the measuring probe. The boundary 52 represents the border between the electrolyte-deficient region 54 of the filler mass 16 in which all suspended potassium chloride particles have been dissolved and a non-deficient region 56 that still contains potassium chloride particles.

Instead of a suspension of KCl particles, one could also use a near-saturated solution of, e.g., approximately 3-molar concentration of potassium chloride in water. However, this has the disadvantage that the measuring probe will have a shorter operating time, because the initial amount of potassium chloride distributed in the filler mass 16 will be smaller than with an electrolyte in suspension form.

In the example of Figure 1, the frontal boundary 52 of the electrolyte deficient region advances substantially along the lengthwise axis A of the housing 2. After the boundary 52 has reached and already passed the open end 38 of the secondary reference element 8, as illustrated in Figure 1, the interior of the secondary reference element 8 will become deficient in secondary electrolyte 44. This will cause a change in the previously constant potential V_2 of the secondary electrode 40. With a continued use of the

measuring probe, the boundary 52 would advance to the primary reference element 6, where it would cause a change of the potential V_1 of the primary electrode 20.

5 Figure 2 illustrates a measuring probe in which the path for the advancement of the frontal boundary of the electrolyte deficiency has been made significantly longer. The measuring probe has a tubular housing 102 of an electrically insulating material, for example glass or a
10 polymer material such as a polyarylether ketone (PAEK), in particular a polyether-ether ketone (PEEK). An enclosed space 104 in the housing 102 contains a primary reference element 106, a secondary reference element 108, as well as an electrolyte 110. An end portion 114 of the housing 102 has
15 an opening 112. The enclosed space 104 is filled with an ion-permeable, high-viscosity, micro-porous polymer substance that forms a filler mass 116 together with the electrolyte 110. Preferably, the filler mass 116 is of the same composition as in the example of Figure 1.

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As illustrated in Figure 2, the primary reference element 106 is configured as a cartridge with an interior tube 118 that runs substantially parallel to the housing 102 and is open at one end, oriented so that the open end 120 of
25 the interior tube 118 faces in the opposite direction from the opening 112 of the measuring probe housing 102. The primary reference element contains a primary electrode 122

with a known electrode potential. In the illustrated example, the primary electrode is an Ag/AgCl electrode with a silver wire 124 that is chlorided at the end and immersed in a primary electrolyte 126. To prevent the primary
5 electrolyte 126 from running out of the open end 120 of the interior tube 118, the electrolyte is enclosed in the pores of an ion-permeable, micro-porous polymer substance, preferably the same as in the filler mass 116. The chlorided end portion 128 of the silver wire 124 is arranged
10 advantageously in the proximity of the closed end 130 of the interior tube 118. A wire lead 132, e.g. a platinum wire, connects the silver wire 124 to an external plug-in contact 138 by way of a seal 136, for example a glass or plastic seal, in the header part 134 of the housing 102.

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The secondary reference element 108 is arranged near the open end of the interior tube 118 and has a secondary electrode 140 with a silver wire 142 that is chlorided at its end portion. The chlorided silver wire is immersed in a part
20 of the primary electrolyte 126 that is near the open end 120 of the interior tube 118. Thus, the primary electrolyte in this case also serves as secondary electrolyte. The secondary electrode 140 is connected to an external plug-in contact 146 by a wire lead 144 running through the seal 136
25 in the header part 134 of the housing 102.

In the example of Figure 2, the electrolyte-deficient region advances from the opening 112 along a path that first leads upward to the open end of the interior tube 118, then turns into the downward direction and continues all the way through the interior tube into the area near the closed end 130. Figure 2 illustrates a situation where the frontal boundary 148 of the electrolyte-deficient portion has already progressed to the inside of the interior tube 118.

As an alternative to the foregoing arrangement, Figure 3 illustrates a configuration where the secondary electrode 140a is arranged outside of the cartridge tube 118. Preferably, the silver wire 142a with the chlorided end portion is immersed in a part of the electrolyte 110 immediately outside the open end 120 of the interior tube 118.

In place of the wire electrodes shown in the drawing figures, one could use electrodes in the form of conductive tracks, a concept that is known per se. In any one of the foregoing embodiments, such tracks could be deposited on the inner or outer wall surface of a cartridge-shaped reference element or on the inside wall surface of the probe housing.

In addition to the foregoing embodiments, which are designed for the measurement of ion concentrations or redox potentials, it is also possible to incorporate the inventive

measuring probe in a single-rod measuring chain. In this case, a measuring electrode, e.g., a pH electrode, needs to be added to the measuring probe. As a preferred configuration, the measuring electrode is arranged as a central tube running lengthwise inside a ring-shaped reference electrode as shown, e.g., in Figure 4 of DE 34 05 431 C2.

Under the inventive method, the remaining operating time of the measuring probe of Figure 2 is determined in accordance with the immediately following description. The method is applicable analogously to other measuring probes of the same general type.

In working with the measuring probe, the primary reference element 106 is used in a conventional manner to perform a potentiometric measurement according to a given procedure; for example in a process-monitoring and/or process-control application. The potential V_1 of the primary electrode 122, since it serves as the reference potential for the measurement, should be as constant as possible. However, this condition is no longer met when the frontal boundary surface 148 of the electrolyte-deficient region has arrived at the primary electrode 122. In order to provide sufficient advance warning of this undesirable event, the invention proposes the concept of monitoring the potential V_2 of the secondary electrode 140 or, more specifically, of the

potential difference $V_{12} = V_1 - V_2$. The monitoring of V_{12} can be performed continuously or at intermittent time intervals, for example periodically.

5 Figure 4 illustrates an example for the potentials V_1 and V_2 as well as the potential difference V_{12} as functions of the elapsed operating time t of the measuring probe of Figure 2. The graphs show a pattern of three distinctive time segments A, B and C, which can be explained as follows.

10 Following the time $t=0$ when the new or regenerated measuring probe has been put into operation, the deficiency boundary 148 is located in the immediate vicinity of the opening 112. If the primary electrode 122 and the secondary
15 electrode 140 are of a substantially identical configuration, their respective potentials V_1 and V_2 will be approximately equal and the potential difference V_{12} will be negligibly small. In practice however, at least a small difference V_{12} will exist already at the beginning because of certain
20 differences between the primary electrode and the secondary electrode. In the example of Figure 4, both V_1 and V_2 are initially negative, and the potential difference V_{12} has a negative value V_A . As long as the deficiency boundary 148 is located in the area between the opening 112 and the secondary
25 electrode 140, the potentials V_1 and V_2 as well as the potential difference V_{12} remain substantially constant. This

situation is characteristic of the time segment A in Figure 4.

After a certain length of operation of the probe, as the deficiency boundary approaches the secondary electrode 140, the potential V_2 of the secondary electrode begins to change and then takes on a new, substantially constant value after the deficiency boundary has passed beyond the secondary electrode. In the example of Figure 4, the new value of V_2 is positive. At the same time, the potential difference V_{12} goes through a first step-like transition from the initial value V_A to a new value V_B . During the subsequent time interval B, the potential difference V_{12} remains substantially constant. The deficiency boundary 148 is located in the area between the secondary electrode 140 and the primary electrode 122 during this time interval. This corresponds to the situation shown in Figure 2.

When the deficiency boundary 148 reaches the primary electrode 122, a change occurs in the potential V_1 . In the illustrated example, the change has the form of a step-like increase. As a consequence, the potential difference V_{12} undergoes a corresponding change which, in the example of Figure 4, manifests itself as a second step-like transition from the value V_B to the value V_C .

As can be concluded from the foregoing example, the first step change in the potential difference V_{12} indicates that the deficiency boundary has reached the secondary electrode and can thus serve as an advance warning for the impending undesirable change of the primary electrode potential. The advance warning occurs with an advance warning time substantially equal to the time interval B. The time interval B depends on the one hand on the distance L by which the two reference elements are offset from each other and on the other hand on the speed at which the deficiency boundary advances. The speed of advancement, in turn, depends on material properties and on the operating conditions of the measuring probe.

In the operation of the measuring probe, the potential difference V_{12} is monitored against a predefined tolerance criterion. When the potential difference V_{12} ceases to meet the tolerance criterion, a base time period t_0 is determined as the elapsed operating time from the point when the probe was put into operation. In accordance with its purpose, the tolerance criterion is set so that the violation of the criterion occurs approximately at the time when the front of the electrolyte-deficient region arrives at the secondary electrode. With regard to the example of Figure 4, the tolerance criterion would thus be set so that the violation of the criterion occurs in the area of the first step change of the potential difference V_{12} . After the base

time length t_g has been determined, the remaining operating time Δt_R of the measuring probe is calculated as a function of the base time length. Consistent with the inventive concept, the calculation is designed so that at the end of the
5 remaining operating time Δt_R , i.e., at the time $t_A = t_g + \Delta t_R$, the front of the electrolyte-deficient region has not yet advanced to the primary reference element, i.e., the undesirable change of the potential V_1 has not yet occurred. Thus, in regard to the example of Figure 4, the remaining
10 operating time Δt_R should definitely not be longer than the time interval B.

To ensure that the measuring probe works in a reliable manner, appropriate steps such as replacing the
15 probe or regenerating the filler mass should be taken after the end of the base time period and in no event later than the end of the remaining operating time Δt_R . As a preferred feature, the violation of the tolerance criterion triggers a warning signal, for example in the form of an optical and/or
20 acoustical indication that servicing measures are required. It is particularly advantageous if the remaining operating time is indicated together with the warning signal, so that a currently running process can be completed according to plan before the servicing measures are initiated.

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The following discussion leads to advantageous operational definitions of the tolerance criterion and to

procedures for calculating the remaining operating time. The definitions are based, among other factors, on monitoring certain quantities over time. Although these time-dependent quantities will in the following context be discussed as
5 continuous functions, the conclusions apply analogously to functions whose values are determined at discrete individual points. In particular the term "time derivative" in the sense of a differential quotient as used below in reference to continuous functions should be understood as difference
10 quotient when referring to discretely tabulated functions. An analogous understanding of the terms applies to signal-smoothing and signal-filtering processes.

In principle, the violation of the tolerance
15 criterion could be defined as the point at which the potential difference V_{12} passes above or below a predefined tolerance value. However, it needs to be taken into account that the potential difference can at the outset be positive or negative, depending on the respective types and individual
20 characteristics of the primary and secondary electrode. Furthermore, the first step change of the potential difference can lead to positive or negative values, and the absolute amount $|V_{12}|$ of the potential difference can increase or decrease. It is therefore appropriate to use the
25 departure of the absolute amount $|V_{12}|$ from a predefined tolerance range as a monitoring criterion. In principle, the tolerance range can be defined through predetermined values

of an upper tolerance limit V_o and a lower tolerance limit V_u . As an alternative, the tolerance range is matched to the initial value of the absolute amount $|V_{12}|$ of the potential difference. In the example of Figure 5, the tolerance range is defined as a tolerance band that is centered on the initial value $|V_A|$ of the absolute amount $|V_{12}|$. The base time period t_g is determined as the elapsed operating time up to the point at which $|V_{12}|$ runs outside the tolerance range. In the case of Figure 5, this is where $|V_{12}|$ traverses the upper tolerance limit V_o . However, it needs to be emphasized that the arrival of the deficiency boundary at the secondary electrode can also cause a reduction of the potential difference V_{12} , particularly in a case where the reference elements are configured differently from each other and have significantly different initial potentials V_1 and V_2 . In this case, the first step change would lead to smaller values of the absolute amount $|V_{12}|$ of the potential difference and would therefore cause the absolute amount $|V_{12}|$ to fall below the lower tolerance limit V_u .

As a further possibility, the base time period t_g can be determined by following the first time derivative dV_{12}/dt of the potential difference (hereinafter referred to as V_{12}') or, more specifically, its absolute amount $|V_{12}'|$. As the first time derivative represents the rate of change of a function, the value of the first time derivative is substantially zero as long as the function stays at an

approximately constant value. In areas where the function undergoes a step change, the first time derivative passes through a maximum or minimum. The absolute value of the first time derivative will in this case peak at a maximum

5 value, independent of whether the step change represents an increase or decrease in the value of the function. Figure 6 represents a time graph of the absolute amount $|V_{12}'|$ of the first time derivative of the potential difference V_{12} , where the peak value of $|V_{12}'|$ corresponds to the steepest part in
10 the area of the step change of the potential difference. The point of violation of the tolerance criterion is appropriately defined as the moment where the absolute amount $|V_{12}'|$ of the first time derivative of the potential difference runs above a predefined tolerance value V_0' .
15 However, the condition for violating the tolerance criterion can also be defined, e.g., by requiring the absolute amount $|V_{12}'|$ of the first time derivative of the potential difference to first rise above a first tolerance value V_0' and to subsequently fall below a second tolerance value V_u' .

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It follows directly from the foregoing discussion that one could also work with the absolute amount $|V_{12}''|$ of the second time derivative instead of the absolute amount $|V_{12}'|$ of the first time derivative. Figure 7 represents a
25 graph of the absolute amount $|V_{12}''|$ of the second time derivative of the potential difference for a time segment around the first step change of the potential difference V_{12} . The dip to zero between the two peak values of $|V_{12}''|$

corresponds to the inflection point in the area where the potential difference passes through the step change.

The point of violation of the tolerance criterion is
5 appropriately defined as the moment where the absolute amount
| V_{12}'' | of the second time derivative of the potential
difference runs above a predefined tolerance value V_0'' .
However, as mentioned above, the condition for violating the
tolerance criterion can also be defined, e.g., by requiring
10 the absolute amount | V_{12}'' | to traverse two or more tolerance
values.

In principle, the remaining operating time Δt_r could
be set independently of the base time period t_g , e.g., by
15 using a predefined reference value based on past experience.
However, there is a significant advantage in calculating the
remaining operating time Δt_r as a function of the base time
period t_g , for example by multiplication with a predefined
factor. This offers in particular the opportunity of taking
20 the current operating conditions into account as they could,
e.g., cause an exceptionally fast or slow advancement of the
frontal boundary of the electrolyte deficiency.

The multiplication factor m needs to be selected so
25 that when the calculated remaining operating time has
expired, the front of the electrolyte deficiency has not yet
arrived at the primary reference element. As an approximate

upper limit for the multiplication factor m , one could use in particular the ratio L_{21}/L_{02} between the path length L_{21} from the secondary electrode 140 to the primary electrode 122 and the path length L_{02} from the opening 112 to the secondary electrode 140. The term "path length" in the present context is not necessarily equal to the geometric distance between the respective locations but represents the effective path length traveled by the boundary 148 of the electrolyte-deficient region. As a safety measure, the multiplication factor m should be chosen smaller than the aforementioned path length ratio, for example 90% of the ratio. Of course, this does not preclude a choice of the multiplication factor that is based on past experience.

To guard against a continued use of the measuring probe after failing to notice a change of the potential V_1 , an additional measure of safety can be achieved by continued monitoring under an alarm criterion after the threshold of the tolerance criterion has been traversed. By setting the remaining operating time to zero when a violation of the alarm criterion has been detected, the operator or the process-control unit can be given a signal that the results delivered by the measuring probe are no longer reliable. The alarm signal can in particular have the form of a message that servicing measures are required immediately. The operational definitions for the alarm criterion can be analogous to those for the tolerance criterion, because it

likewise involves the process of detecting a step change of the potential difference V_{12} . Consequently, the alarm criterion can again be based on the absolute amount of either the potential difference itself or on the absolute amount of the first or second time derivative of the potential difference.

It is particularly advantageous to monitor the measuring probe under the alarm criterion if the calculation of the remaining operating time Δt_r appears doubtful, for example in a case where no reference values from past experience are available for the selection of the multiplication factor m , or if the speed of advancement of the deficiency boundary is variable or unknown because of variable or unknown operating conditions.

The monitoring phase under the alarm criterion is also advantageously used in pre-trial experiments with a given type of measuring probe. In this case, the calculated remaining operating time is ignored and the operation of the measuring probe is continued up to the point where the alarm criterion is actually violated in order to gain reference values for the calculation of the remaining operating time.

The time graphs in Figures 4 to 7 are idealized insofar as in certain applications, the signal contains an additional fluctuation or noise component. This unwanted

portion of the signal manifests itself even more strongly in the time derivatives, i.e., the signal-to-noise ratio deteriorates progressively with higher-order derivatives. To prevent the risk that a momentary fluctuation of the
5 monitored quantity $|V_{12}|$ or $|V_{12}'|$ or $|V_{12}''|$ could cause a premature violation of the tolerance criterion or alarm criterion, it is appropriate to use signal-filtering in the monitoring of the potential difference. Depending on the measuring principle used in the monitoring process, an analog
10 or digital filtering method can be used.

Clearly, the apparatus according to the invention has useful applications in process-monitoring and/or process-control. By offering a way of preventing the measuring error
15 due to the electrolyte deficiency, the concept of determining the remaining operating time of the potentiometric measuring probe significantly contributes to the safety of a process.

List of Reference Numbers

2	Housing
4	Enclosed space in 2
6	Primary reference element
8	Secondary reference element
10	Electrolyte
12	Opening in 2
14	End portion of 2
16	Filler mass
18	Cartridge of 6
20	Primary electrode
22	Chlorided silver wire of 20
24	Primary electrolyte
26	Open end of 18
28	Conductor lead for 20
30	Plug-in contact for 28
32	Header of 2
34	Sealing plug of 18
36	Cartridge of 8
38	Open end of 36
40	Secondary electrode
42	Chlorided silver wire of 40
44	Secondary electrolyte
46	Conductor lead for 40
48	Plug-in contact for 46
50	Sealing plug of 36
52	Boundary of electrolyte-deficient region
54	Electrolyte-deficient region of 16
56	Non-deficient region of 16
102	Housing
104	Enclosed space of 102
106	Primary reference element
108, 108a	Secondary reference element
110	Electrolyte

112	Opening of 102
114	End portion of 102
116	Filler mass
118	Interior tube
120	Open end of 118
122	Primary electrode
124	Chlorided silver wire of 122
126	Primary electrolyte
128	Chlorided end portion of 124
130	Closed end of 118
132	Conductor lead for 122
134	Header of 102
136	Seal of 102
138	Plug-in contact of 132
140, 140a	Secondary electrode
142, 142a	Chlorided silver wire of 140
144	Conductor lead for 140
146	Plug-in contact for 144
148	Boundary of electrolyte-deficient region
A	Longitudinal axis of 2
L	Lengthwise offset between 6 and 8
V_1	Potential of the primary electrode
V_2	Potential of the secondary electrode